Data Validation Standard Operating Procedures for

Chlorinated Dioxin/Furan Analysis by High Resolution Gas Chromatography/

High Resolution Mass Spectrometry

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 4

SCIENCE AND ECOSYSTEM SUPPORT DIVISION
MANAGEMENT and TECHNICAL SERVICES BRANCH
QUALITY ASSURANCE SECTION

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1. Objective

The objective of this Standard Operating Procedure (SOP) is to assist in the technical review of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) analytical data. This SOP is presented to help clarify and augment the review guidance of the *National Functional Guidelines for Chlorinated Dioxin/Furan Data Validation, September 2005*, which are applied by Region 4, not only for data generated under the DLM contract series, but for all dioxin/furan contract data, specific method requirements notwithstanding. It provides guidance for areas of data review that require considerable professional judgment, and to specify procedures that are unique to the needs of Region 4. The document also defines the formats of data review reports and the data entered into the Region 4 LIMS (Element®). This document does not discuss risk assessment and the user must seek other assistance in this area. In addition, determining contract compliance is not the intended objective of these guidelines.

2. Applicability

This SOP is applicable to CDD/CDF data collected from environmental sample matrices using a high resolution gas chromatograph and high resolution mass spectrometry (HRGC/HRMS) method. This SOP is based on the quality assurance and quality control (QA/QC) requirements specified in Exhibit D of DLM02.0 of the Field Analytical Services Technical Advisory Committee (FASTAC) *USEPA Statement of Work (SOW) for Analysis of Chlorinated Dibenzo-p-dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs), Multi-Media, Multi-Concentration, Solicitation Number PR-HQ-00-11943, May 2005,* as well as the additional requirements for Region specified in the Dioxin Analytical Services Client Request Form submitted to the laboratories for the CDD/CDF projects. From time to time, Region 4 also reviews data generated by EPA Method 1613B (October 1994) and EPA SW846 Method 8290A (February 2007). The specified QA/QC requirements in these methods, typically a subset of the requirements under the FASTAC protocols, will be used for data quality evaluation. In addition, project-specific data generation and quality assessment criteria may also apply and will be utilized in conjunction with this SOP.

3. Data Qualifier and Remark Definitions

Region 4 applies two sets of qualifiers for the CDD/CDF data. The primary qualifiers are those defined in the SOW DLM02.0, while a secondary set of qualifiers is used in Region 4 to provide more information for data users on the specific circumstances leading to data qualification. Both primary and secondary data qualification codes appear in the data review report and in the Region 4 LIMS Element®. The definitions and brief explanations of the qualifiers and remarks assigned to results in data validation process are presented in Attachments I and II.

4. Holding Times

The holding times for extraction/preparation presented in Exhibit D of DLM02.0, Section 8.3.1 are considered contractual holding times only and are not to be considered for technical qualification of analytical data.

The most recent guidance available (Method 1613B) indicates that there are no demonstrated maximum holding times associated with the extraction/preparation of CDDs/CDFs in aqueous, solid, semi-solid, tissues, and other sample matrices. If samples are stored properly, the holding times for extraction/preparation are up to one year. Aqueous, solid, semi-solid samples should be stored in the dark at 0-4 ^{o}C. Tissue samples should be stored in the dark at less than -10 ^{o}C and if properly stored in the dark at less than – 10 ^{o}C, sample extracts may be stored up to one year.

If residual chlorine is present in potable water and municipal waste water samples, dechlorination should be performed and documented.

Action:

If the holding times specified in Method 1613B for extraction and/or for analysis of sample extracts are exceeded, positive results are considered to be estimated (J flag) and non-detects are considered to be unusable (R flag). Temperature excursions during shipment of aqueous, solid, semi-solid or tissue sample matrices do not typically require action; however, use professional judgment if the temperature excursion is unusually high or is for an extended time.

5. System Performance

Demonstration of system performance is a fundamental requirement for any laboratory using DLM02.0 and other High Resolution Mass Spectrometry (HRMS) methods [e.g., Method 1613 (Revision B) or SW-846 Method 8290A (Revision 1)]. If mass calibration and resolution tuning is not correctly performed, interferences may degrade chlorinated dibenzo-p-dioxin and chlorinated dibenzofuran (CDD/CDF) identification and quantitation. Mass calibration and resolution is the first part of the three fundamental High Resolution Gas Chromatography/HRMS (HRGC/HRMS) system performance checks. The second fundamental performance check is the Window Defining Mixture (WDM) for the mass spectrometer Selected Ion Monitoring (SIM) scan descriptor switching times. The third fundamental performance check is Gas Chromatographic (GC) resolution.

1. Mass Calibration and Mass Spectrometer Resolution

Criteria:

Review the hardcopy of Mass Spectrometer resolution demonstration. Laboratories are required to provide evidence of Mass Spectrometer resolution > 10,000 at the beginning **and end** of each 12-hour analytical sequence. Documentation of Mass Spectrometer resolving power must include a hardcopy peak profile of a high-mass reference signal from PFK (e.g., m/z 380.9760) obtained during the peak matching experiment, with another high-mass ion (e.g., m/z 304.9824) as the reference mass. The selection of the low- and high-mass ions must be such that they provide the largest voltage jump in the descriptor group. This demonstration may be performed on any of the five mass descriptors. The format of the peak profile representation must allow manual verification of Mass Spectrometer resolution [i.e.,

the horizontal axis must be a calibrated mass scale (amu or ppm per division)]. The result of the peak width measurement must appear on the hardcopy. Most laboratories include documentation of resolving power for each descriptor channel.

The deviation between the exact m/z and the theoretical m/z monitored must be < 5 ppm. In other words, the maximum of the peak matching profile must be within the 5 ppm range shown at the top of the window. If there was not enough PFK in the system, the profile peaks may not fill the window, but should be Gaussian shaped and centered in the window. If the system is very noisy and the profile is covered with spikes, it may be very difficult to evaluate performance. If the laboratory has included information for all descriptors, examine each to determine whether only a single descriptor or the entire system is subject to noise.

Action:

Mass Spectrometer resolution is critical to the success of this method of CDD/CDF analysis. In the event that Mass Spectrometer resolution is < 10,000, or there is evidence of system noise, the evidence provided must be carefully evaluated, and additional information requested as needed. If only one or two out of five descriptors show resolution < 10,000, the reviewer may consider qualifying only associated results as unusable (R flag). However, if the majority of the descriptors show significant system noise, or resolution < 10,000, qualify all associated data as unusable (R flag).

2. Window Defining Mixture

Review the Form(s) 5DFA (Form V-HR CDD-1). Prior to the calibration of the High Resolution Gas Chromatograph/High Resolution Mass Spectrometer (HRGC/HRMS) system, the laboratory must establish the appropriate switching times for the Selected Ion Monitoring (SIM) descriptors and verify the chromatographic resolution. The switching times are determined by the analysis of the Window Defining Mixture which contains the first and last eluting isomers in each homologue (level of chlorination) series. Chromatographic resolution is verified by analyzing one of two Isomer Specificity Check (ISC) solutions, depending on the Gas Chromatograph (GC) column used for analysis. The WDM and ISC can be combined in a single Column Performance Solution (CPS) analysis at the discretion of the analyst. The 12-hour time period begins with the injection of the WDM or CPS.

Criteria:

The WDM must be analyzed after the PFK tune and before any calibration standards on each instrument and GC column used for analysis, once at the beginning of each 12 hour period during which standards or samples are analyzed and whenever adjustments or instrument maintenance activities are performed that may affect Retention Times (RT).

Verify that the WDM was analyzed at the required frequency. Examine the WDM chromatograms to determine when descriptor switching times are turned on and off. Note the RT of each first and last eluting isomer in each homologue for identification of switching times. In particular, note the presence of the last eluting tetra congener, 1,2,8,9-TCDD, and the first-eluting PCDD congener, 1,3,4,6,8-PCDD, since these compounds normally elute

within 15 seconds of each other on the DB-5 column. Each positive dioxin and furan result (tetra- through hepta-) must have an RT within the limits established by the WDM for the corresponding homologue. The 2,3,7,8-substituted dioxins and furans must also meet the Relative Retention Time (RRT) limits in the SOW.

Action:

If the WDM was not analyzed at the required frequency or correct settings of descriptor switching times are not evident, but the calibration standards met specifications the individual 2,3,7,8-substituted target analyte, results may be usable without qualification. If the WDM fails and the laboratory did not take appropriate corrective action and/or chromatography for the calibration standards indicates a significant problem with descriptor switching times, first verify that all associated 2,3,7,8-substituted congeners are present in each descriptor. If this is the case, but the WDM failed to include all members of each homologous group, qualify data for all homologue totals as unusable (R flag). If not all of the 2,3,7,8-substituted homologues are present in the associated descriptor, qualify all data as unusable (R flag). Notify the Task Order Project Officer (TOPO) if any of these problems are evident, to decide if sample reanalysis is necessary.

3. Chromatographic Resolution

Evaluate the ability of the Gas Chromatograph (GC) column to resolve the closely eluting dioxin and furan isomers by reviewing Form 5DFB (Form V-HR CDD-2), and the corresponding Selected Ion Current Profile (SICP) of each isomer and each of the analyses reported on Form 5DFB. An evaluation must be made for each column used in the analysis of samples. Different evaluation mixtures are used for the three common columns (see Table 5, p. 4-70/76 of DLM02.0).

Criteria:

For the DB-5 (or equivalent) column, the chromatographic peak separation between the 2,3,7,8-TCDD peak and the 1,2,3,8-TCDD peak must be resolved with a valley of $\leq 25\%$ using the following equation:

$$\text{Valley} = x/y * 100$$

Where,
x = The measurement from the baseline to the deepest part of the valley between 2,3,7,8-TCDD and 1,2,3,8-TCDD, and
y = The peak height of 2,3,7,8-TCDD

Chromatographic resolution criteria for the DB-225 (or equivalent) column are that the peak separation between the 2,3,7,8-TCDF peak and the 2,3,4,7-TCDF peak must be resolved with a valley of # 25% using the equation above.

Further analysis may not proceed until the GC resolution criteria have been met. The identical HRGC/HRMS conditions used for the analysis of the WDM, ISC, and CPS solutions must

also be used for the analysis of the initial calibration and calibration verification solutions. Analysis on a single GC column (as opposed to situations requiring second column confirmation) is acceptable if the required separation of all of the 2,3,7,8-substituted isomers is demonstrated and the resolution criteria for both the DB-5 and DB-225 (or equivalent) columns are met, as stated above.

Manually check at least one GC resolution demonstration (check more if more than one analyst appears to have contributed or if problems are noted).

Action:

If the GC resolution does not meet the specifications, qualify all detects and non-detects for 2,3,7,8-TCDD and/or 2,3,7,8-TCDF, whichever failed, as estimated (J flag) and notify the Task Order Project Officer (TOPO) to decide on sample reanalysis.

Table I System Performance Checks

Criteria	Action
Mass Spectrometer resolution of ≥10,000 is not demonstrated	R
WDM fails, or WDM is not reported	J-2,3,7,8, R-homologue totals
WDM fails, and WDM adjustments are not made, and Calibration standards indicate a problem in detecting 2,3,7,8-substituted congeners because of gross errors in the scan descriptor times	R
CPS fails or is not reported	J

6. Initial Calibration

Initial calibration of the HRGC/HRMS system must be performed on a compliant system, or one that has been shown to meet all of the previously discussed performance criteria. The data package should contain Form 6DFA (Form VI-HR CDD-1), Form 6DFB (Form VI-HR CDD-2), and raw data for all standards.

Criteria:

1. Ion abundance criteria: The relative ion abundance criteria for chlorinated dibenzo-p-dioxins/ chlorinated dibenzofurans (CDDs/CDFs) must be met for all CDD/CDF peaks, including the isotope-labeled peaks, in all solutions. The lower and upper limits of the ion abundance ratios represent a ± 15% window around the theoretical abundance ratio for each pair of selected ions. Please note that the $^{37}Cl_4$-2,3,7,8-

TCDD clean-up standard contains no ^{35}Cl, therefore the ion abundance ratio criteria do not apply to this compound. Check the calculation of at least one target analyte in one initial calibration for each analytical column.

2. Retention Time (RT) criteria: For all calibration solutions, the RTs of the isomers must fall within the appropriate RT windows established by the WDM analysis. In addition, SOW DLM02.0, Exhibit D, Section 9.3.5.5 (§10.2.4 of Method 1613B) requires that the absolute RT of the internal standard $^{13}C_{12}$-1,2,3,4-TCDD must exceed 25 minutes on the DB-5 (or equivalent) column and 15 minutes on the DB-225 (or equivalent) column. Method 8290A does not contain a minimum retention time requirement, only resolution performance criteria in §9.3.1.

3. Mass Spectrometer sensitivity criteria: For all calibration solutions, including the CS1 solution, the S/N ratio must be > 10:1.

4. Linearity criteria: The RRFs and Percent Relative Standard Deviation (%RSD) of the five RRFs (CS1-CS5) for each compound applicable to RRF (internal standard) treatment is calculated. The %RSD of the five RRFs (CS1-CS5) must not exceed 35% for these compounds. Likewise, the RR and %RSD of the five RRs (CS1-CS5) for each compound applicable to RR (isotope dilution) treatment is calculated. The %RSD of the five RRs (CS1-CS5) must not exceed 20% for these compounds.

5. Concentration criteria: All initial Calibration Standards (CS) must be analyzed at the correct concentration levels (see SOW).

6. Frequency criteria: Each HRGC/HRMS system must be initially calibrated to meet the terms of the contract whenever the laboratory takes corrective action which may change or affect the initial calibration criteria, or if the calibration verification (CS3 calibration verification) acceptance criteria cannot be met even after corrective action.

Action:

1. All initial calibration standards must be analyzed at the concentrations described in the DLM02.0 SOW. Initial calibrations must be performed when the contract is awarded, whenever significant instrument maintenance is performed (e.g., ion source cleaning, GC column replacement, etc.), or if calibration verification criteria are not met.

2. If an analyte in a calibration standard failed the ion abundance ratio criteria, qualify sample results analyzed immediately after that initial calibration using the RR, RRFs or values for quantitation as unusable (R flag) for that analyte, because both the RRF and RR values depend on the areas used in the ion abundance ratio. Failed ion abundance ratio criteria for any analyte is a cause for concern, and may indicate that the Mass Spectrometer is not tuned correctly, the zero point is not correctly adjusted, or other problems.

3. Use professional judgment for a more in-depth review to minimize the qualification of data which may be accomplished by considering the following hypothetical examples:

   a. If the ion abundance ratio is not within the limits for an analyte in the CS1 solution, qualify the low-end results for that analyte (below the CS2 concentration) as unusable (R flag).

   b. If the ion abundance ratio is not within the limits for an analyte in the CS5 solution, qualify the high-end results for that analyte (above the CS4 concentration) as unusable (R flag).

4. If the %RSD is not within ± 20% and ± 35% for the RR and RRF, respectively, qualify the detects as estimated ("J" flag). The reviewer may discard either the CS1 or CS5 values for the initial calibration and recalculate the %RSD. If discarding either of these points brings the %RSD within the specified limits, qualify either the low- or high-end hits, depending on which point was discarded. Use professional judgment to request reanalysis if either of these scenarios affects a majority of the data.

5. The situation when the S/N ratio 10:1 sensitivity requirements are not met usually occurs for the low standard (CS1). In these instances, consider dropping the lowest calibration point and qualifying any results less than the CS2 standard as estimated ("J" flag). If problems with noise affect more than the low level standard, reanalysis should be requested, or the associated data may need to be rejected (R flag).

6. If retention time criteria are not met for an initial calibration, all non-detect results should be considered suspect and qualified as rejected (R flag). The TOPO should be contacted to request a re-analysis of the associated samples.

Table II Initial Calibration

Criteria	Action:	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
Initial calibrations are not performed at the prescribed concentration and frequency	R	UR
Ion Abundance Ratios is not within ± 15% of theoretical values, as described in Table A.4	R	UR
GC Resolution (% Valley) of > 25%	J	No qualification
Linearity: RRF %RSDs is not within ± 35%; RR %RSDs is not within ± 20%	J	UJ
Sensitivity < 10:1 S/N ratio for all SICPs	J	UJ
RTs: Not within appropriate windows	See Action section for WDM, above	No qualification

7. Calibration Verification

A midrange (usually CS3) standard must be successfully analyzed at the beginning of each 12 hour analysis period, after the WDM and resolution standard(s) and before any samples or method blanks are analyzed. Calibration verification is used to validate the initial calibration on which quantitations are based, and to check for satisfactory stability and performance of the instrument. The CS3 standard is used as a measure of instrument stability, including the evaluation of Gas Chromatograph (GC) Retention Times (RTs), relative ion abundance criteria, sensitivity, and the calibration criteria for Relative Responses (RRs) and Relative Response Factors (RRFs). Review the Form 7DFA (Form VII-HR CDD-1), Form 7DFB (Form VII-HR CDD-2), and raw data from the midpoint (CS3) standard.

Criteria:

1. Absolute RT criteria: For Region 4 data, the absolute RT of the first internal standard $^{13}C_{12}$-1,2,3,4-TCDD should be within ± 15 seconds of the absolute RT of the identical compound obtained during initial calibration. SOW DLM02.0 requires that if the RT of the first internal standard changes by more than ± 15 seconds, the laboratory must adjust the switching times of the descriptors and analyze the Window Defining Mixture (WDM) before proceeding with further analyses. Additionally, for contracts using Method 1613B or SOW DLM02.0, the absolute RT of the aforementioned first internal standard must exceed 25.0 minutes on the DB-5 column, and 15.0 minutes on the DB-225 column.

2. Relative Retention Time (RRT) criteria: The RRTs of the native and labeled chlorinated dibenzo-p-dioxins/chlorinated dibenzofurans (CDDs/CDFs) must be within the limits described in the SOW.

3. Ion abundance ratio criteria: All native and labeled CDDs/CDFs in the CS3 standard must be within their respective ion abundance ratio limits.

4. Instrument sensitivity criteria: The peaks representing both native and labeled analytes in the CS3 standard must have signal-to-noise (S/N) ratios ≥10:1.

5. Response criteria: The measured RRFs and RRs of each analyte and standard (labeled and internal) must be within ± 20% (RR) and ± 35% (RRF) of the mean values established during initial calibration. Check the calculation of at least one target analyte in a calibration verification standard for each analytical column used.

Action:

1. Use professional judgment to qualify any analyte in samples associated with a calibration verification not meeting the RT and/or RRT criteria. If the absolute RT in the standard is >15 seconds different from the initial calibration, the homologue totals may need to be qualified "R" even if all target analytes are identified.

2. Any detect in samples associated with a calibration verification not meeting the ion abundance criteria should be evaluated very carefully. Consider peak shapes in the standard and in the samples, the stability of the lock mass trace, and the level of background signal in standards and samples. If these sources indicate that system performance was degraded when the calibration was run, data for associated analytes should be qualified as rejected (R flag). If this evaluation indicates that the standard was affected by a transient interfering baseline shift, it may be more appropriate to apply the "J" or estimated flag.

3. If the S/N ratio≥10:1 limit is not met in a calibration verification, qualify all detects as estimated (J flag) and all non-detects as unusable (UR flag).

4. Since the initial calibration is used to generate the RR and RRF values used for quantitation, the %D relative to the Mean RR or Mean RRF of the initial calibration is an important criterion for review. Qualify data associated with an analyte with a %D not within ± 20% (RR) and not within ± 35% (RRF) as estimated (J flag). Re-analysis of the samples may be requested.

Table III Calibration Verification Decision Matrix

Criteria	**Action**	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
Ion abundance ratios not within ± 15% window	R or J	UR or UJ
Absolute RT of internal standard $^{13}C_{12}$-1,2,3,4-TCDD > 25 minutes on DB-5 (or equivalent) column, or > 15 minutes on DB-225 (or equivalent) column	Use professional judgment	
Internal standards in the calibration verification not within 15 seconds of the RTS in the initial calibration	Use professional judgment, qualify homologue totals R	
RRTs in the calibration verification not within the limits defined in SOW	Use professional judgment	
Sensitivity: S/N < 10	J	UR
%D for RRs not within ± 20% %D for RRFs not within ± 35%	J	No qualification

8. Method Blank Analysis

One or more method blanks should be extracted with each batch of samples (one for each extraction batch). The matrix for the method blank should be similar to the associated samples. The associated method blank and the blind blank should be evaluated for contamination.

Criteria:

Laboratory method blanks should not contain any 2,3,7,8-substituted CDDs/CDFs with the exception of OCDD/OCDF, in amounts greater than the CRQL. No OCDD/OCDF should be present in amounts greater than three times (3X) the CRQL.

Action:

1. Action in the case of blank contamination depends on the circumstances and origin of the blank. Qualification of the sample data should be based upon comparison with the associated blank having the highest concentration of a contaminant. The laboratory is required to analyze the method blank on each analytical system used to analyze samples. This includes both the DB-5 primary column and the DB-225 confirmatory column whenever any associated samples require 2,3,7,8-TCDF confirmation (either a positive result or an EMPC value exceeds the CRQL). The reviewer should use the highest result from the same column to make decisions about data. Associated blanks include the extraction method blanks and the PES blind blank. Field and equipment blanks are not used for data qualification.

2. Any compound detected in the sample that was also detected in any associated blank is reported as a non-detect if the sample concentration is less than five times (5X) the blank concentration. Typically, the calculated sample CDD/CDF amount above the CRQL is reported and flagged “U” with the secondary qualifier “B-4” in Element®. For results below the CRQL, report in Element® the actual laboratory results with the “U” qualifier only.

3. There may be instances where little or no contamination was present in the associated blanks, but qualification of the sample was deemed appropriate. Professional judgment should be used in these situations. One example would be where the method blank did not satisfy one of the identification criteria, either the 2.5X signal to noise ratio (S/N) requirement, or the ion ratio requirement to report an analyte present, but the actual sample contained the analyte at with acceptable ion ratio, and/or with slightly greater than 2.5X S/N and less than five times the possible blank concentration. An explanation of the rationale used for this determination should be provided in the Summary of Problems and Comments.

4. If gross contamination exists (i.e., saturated peaks), all affected compounds in the associated samples should be considered to be unusable (R flag), due to interference. This is a contract issue and should be regarded as an action item to be reported to the

Task Order /Project Officer (TOPO) for resolution with the contractor.

5. If an instrument blank was not analyzed following a sample analysis which contained an analyte(s) at high concentrations, sample analysis results after high concentration sample must be evaluated for carryover. Professional judgment should be used to determine if instrument cross-contamination has affected any positive compound identification(s).

6. Blanks or samples run after a Performance Evaluation Sample, Laboratory Control Sample or Calibration Verification should be carefully examined to determine the occurrence of instrument or syringe carry-over. Since the efficiency of sample transfer can vary dramatically according to apparatus and operator techniques, professional judgment should be used in each case to determine whether sample or blank results are attributable to carry-over.

7. When there is convincing evidence that contamination is isolated to a particular instrument, matrix, or concentration level, professional judgment should be used to determine if the 5X rule should only be applied to certain associated samples (as opposed to all of the associated samples).

Table IV Method Blank Decision Matrix

Method Blank Result	Sample Result	Action for Samples
<CRQL	Not detected	No action
	<CRQL	Report calculated result value with "U"
	>CRQL	If still < 5 * blank result, qualify as "U" with secondary qualifier "B-4"
≥CRQL	<CRQL	Report calculated result value with "U"
	≥CRQL but <Blank Result	Report calculated result value with "U" with secondary qualifier "B-4"
	≥CRQL and >Blank Result	If still < 5 * blank result, qualify as "U" with secondary qualifier "B-4"
	≥CRQL and > 5* Blank Result	Use professional judgment, may qualify positive results as estimated ("J")
Gross contamination	Positive	Use professional judgment, may qualify all results as unusable ("R")

9. Performance Evaluation Samples

The laboratory must demonstrate its ability to achieve acceptable results through the analysis of Performance Evaluation Samples (PES). PESs will be included with the case at the discretion of the Region. Dioxin PESs include both blank samples and spiked samples.

The PESs are typically scored by utilizing the QATS-SPS software. The QATS-SPS software scoring system is a two-tiered system. The first tier contains data within a statistically established 95% confidence interval or “warning” limit. A second tier contains

the results that fall between the 95% and 99% confidence interval or "action" limit. If the limits are not determined due to the lack of statistical significance, a score of "Not Evaluated" will be given.

Action:

1. SPS Web evaluation – If the analyte is scored by SPS Web as "Within Limits" or "Not Evaluated," no flags are required. If the analyte is scored by SPS Web as "Action Low" or as "Analyte Missed," non-detects for that analyte are rejected (R flag) and positive results are considered estimated (J flag). If the analyte is scored by SPS Web as "Warning Low," both non-detect and positive results for that analyte are considered estimated (J flag). If the analyte is scored by SPS Web as "Warning High" or "Action High," non-detects are not qualified and positive results are considered to be estimated (J flag).

2. The results of the analysis of the PES blank sample are to be included with the method blank(s) to be used in evaluating potential contamination. The same rules for laboratory method blank rules should apply.

3. PESs will be logged into Element® and reported as routine samples. The following conventions apply for entering results into Element®:

    a. Report the PES results on the internal PCDD/PCDF spreadsheet.
    b. Report all results regardless of comparison to any associated blanks.
    c. Report actual values of spiked compounds, using two significant digits but score the three significant digits as reported by lab.
    d. Use the qualifiers reported by the lab. Neither Element® qualifiers nor remarks are required for PES results.
    e. The TEQ values are not evaluated for PES.

Table V PE Sample Data Evaluation Actions

Criteria	Action	
	Detected Associated Compounds	**Non-Detected Associated Compounds**
Results "warning low"	J	UJ
Results "action low"	R	UR
Results "warning high" or "action high"	J	No flag

10. Dilutions

Criteria:

If the concentration of the analyte exceeds the concentration of the highest standard, except for OCDD/OCDF, a dilution should be performed. For dilutions up to 1:20, the laboratory will add solvent to perform the dilution. In accordance with the Region 4 addendum to the DLM contract, additional labeled extraction standard is added by Region 4 laboratories for dilutions up to 1:100, to bring the concentration up to that in the initial extract.

If a simple dilution and re-analysis of the extract has been done, there should be no change in the way results are calculated. This is to say the total picograms of ES in the extract will remain the same.

Whenever additional labeled extraction standard (ES) was added, the total amount of ES present, in picograms, is used to calculate results, rather than the dilution factor. The calculation check should either show the increased total amount of ES or incorporate the dilution factor, assuming the laboratory added a sufficient amount of ES to bring the concentration back to the nominal level (100 pg/ul for tetra – hepta, 200 pg/ul for octa). Under no circumstances should the recovery results, determined from the original extract, be used to correct the dilution results for recovery. Occasionally, the laboratory might be unable to report recoveries due to interferences from co-eluting target or nontarget compounds. All associated positive results will then be "J" qualified and associated non-detected results will be "UR" qualified along with the addition of the "QS-2" Element® qualifier.
The laboratory is required to report both the initial or neat analysis and one diluted analysis. A combination of results from the initial and diluted analyses for one sample on the internal PCDD/PCDF spreadsheet is needed to report analytes within the calibration range, but also to enable the lowest detection limits to be reported for non-detects.

Action:

1. Verify that all reported sample values are within the calibration range by checking against the DL and CL in samples on the PCDD/PCDF spreadsheet.

   For Region 4 reporting purposes, the CRQL, and Calibration Limit (CL) are calculated as follows:

   For water samples:
   CRQL (ng/L) = (CS1 x Ve x DF)/ Vs

   CL (ng/L) = (CS5 x Ve x DF)/ Vs

   For solid samples:
   CRQL (ng/kg) = (CS1 x Ve x DF) / (Vs x (1- M/100) x 1000)

   CL (ng/kg) = (CS5 x Ve x DF) / (Vs x (1- M/100) x 1000)

   Where: CS1 = The lowest standard, ng/mL

CS5 = The highest standard, ng/mL
Ve = the volume of final extract, uL
DF = Dilution Factor (where appropriate)
Vs = Sample volume or amount, g or mL
M = % moisture content

Note: Check the nature of the solid samples used for extraction. If the laboratory uses an aliquot of the dried sample for extraction, no moisture content adjustment is needed.

2. If the laboratory performs a dilution and reports both the initial and diluted analyses, the data reviewer must report those congener values that are within the calibration range. If congener values in the initial analysis exceed the calibration range, report congener values from the diluted analysis. Indicate the congener values reported from the dilution analysis with the qualifier "D" on the PCDD/PCDF spreadsheet. Report non-detect results from the least diluted analysis with acceptable QC.

3. If any reported congener value is above the calibration range of the method, qualify those results as estimated (J flag) with remark "CLP02."

4. If any reported congener value is below the CRQL, qualify that result as estimated (J flag) with remark "CLP01."

5. Element® requires the reported analyte concentration in water in ng/L, while the laboratories might report the units in either pg/L or ng/L. The unit for solid samples is ng/kg for all. Caution must be taken in converting the units of results on the PCDD/PCDF spreadsheet.

11. Labeled Compound Recoveries

Recoveries of the labeled compounds measure the extraction effectiveness of the method.

Criteria:

The percent recovery of any labeled compound in the original sample, prior to any dilutions, must be within the limits specified in Exhibit D, Table 7, of DLM02.0. If the percent recovery is outside the limits, re-extraction and re-analysis of that sample should have been performed by the laboratory.

Action:

1. If the extract is diluted less than 20X with solvent and the concentrations of the labeled compounds are brought back to the initial levels, the dilution factor should be applied to the recoveries of labeled compounds. The recovery has no effect on qualitative identification of the native analyte.

2. If the labeled compound recovery exceeds the upper limit, a positive result of the

associated native analyte in that sample is considered to be estimated ("J" flag with Element® qualifier QS-5).

3. If the labeled compound recovery is equal to or greater than 10% but is less than the lower limit, the result, both non-detect and positive, of the associated native analyte in that sample is considered to be estimated ("J" flag with Element® qualifier QS-3).

4. When the labeled compound recovery is less then 10%, quantitation is severely affected. A positive result of the associated native analyte in that sample is considered to be estimated ("J" flag with Element qualifier QS-4) and a non-detect is rejected ("UR" flag with Element qualifier QS-4).

12. Toxicity Equivalency Factors

The EPA initially adopted dioxin International Toxicity Equivalent Factors (I-TEF/89) for summarizing dioxin concentrations so information could be exchanged consistently within the international scientific community. The I-TEFs/89 are interim in character and may be replaced or modified after further research. Seventeen of the possible 210 chlorinated congeners of dioxin and furan are 2,3,7,8- substituted. The most toxic congener is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). TEFs are used to convert the concentrations of any PCDD/PCDF congeners into an equivalent concentration of 2,3,7,8-TCDD. The congener specific data are multiplied by the appropriate TEFs (separate factors for mammals, birds, and fish) and, assuming the toxic effects are additive, the factors are totaled to obtain a Toxicity Equivalent Quantity (TEQ) for mammals, birds, and fish.

In addition, Region 4 views non-detect results for the toxic PCDD/PCDF congeners as minimum detectable concentrations, and therefore assigns a non-zero TEQ using the reported EDL or EMPC as a surrogate for the non-detect result.

Action:

1. For each 2,3,7,8-substituted CDD/CDF congener, the TEQ is calculated in the same units as for the congener result by multiplying the laboratory result with the corresponding Region 4 adopted TEF to record on the PCDD/PCDF spreadsheet. The sum of all the individual TEQs is then reported as the TEQ for the sample. Currently, the 2005 TEFs from the World Health Organization (WHO) are used for mammalian TEQs, and 1998 WHO TEFs are used for avian and fish TEQs.

2. The method of reporting TEQ values depends on the use of the data for toxicity risk evaluation and could vary from Region to Region. For Region 4, both the non-detect EDLs and all EMPCs will also be multiplied by the TEFs for the purpose of assigning a TEQ, but homologue totals will have no TEQ assigned.

3. For each sample, if more than ten percent of the congener results are assigned the "J," "U," or "R" flag, report the total TEQ value with the "J" flag and Element qualifier D-5.

4. In the event that all target 2,3,7,8-substituted congeners are not detected in a sample, the TEQ totals are reported with a "UJ" flag.

13. Second Column Confirmation

The positive result with concentration above CRQL of 2,3,7,8-TCDF obtained from the primary column must be confirmed by re-analysis of the sample extract on a separate confirmation column that is known to resolve the 2,3,7,8-TCDF from other congeners.

Action:

Due to the resolution capabilities of the primary column for 2,3,7,8-TCDD/TCDF, the results from the confirmation for 2,3,7,8-TCDF are used for reporting on the PCDD/PCDF spreadsheet. However, other factors might also impact on the quality of the data from both columns. The actions taken are summarized in the following table:

Table VI TCDF Confirmation Actions

Primary Column	Confirmation Column	Actions
< CRQL	(Not required)	Report result with "J" and Element® Qualifiers "CLP01,CLP24."
Positive	Positive (could be < CRQL)	Report confirmed value (with "J" for < CRQL) and the Element® qualifier "CLP10" ("CLP01" for < CRQL).
Positive	Non-detect	Unconfirmed. Report EDL with "U."
Positive	EMPC	Report the smaller of the two results with "U, CLP18."
EMPC	Positive (could be < CRQL)	Report confirmed value (with "J" for < CRQL) and the Element® qualifier "CLP10" (and "CLP01" for < CRQL.)
EMPC	EMPC	Report the smaller value of the two results with "U" and the Element® qualifier "CLP18."

14. Data Review Documentation

A Data Review Document should be prepared to present and discuss the CDD/CDF review findings. The document includes the Review Summary Narrative, Summary of Problems and Comments which includes the Blank Summary, the Internal PCDD/PCDF spreadsheet, copies of reviewer's calculations, PE sample scoring results, memoranda detailing any phone

conversations with the laboratory, and copies of any correspondence with Contracts Management Branch detailing any technical or contractual issues raised during review of the CDD/CDF data package. This documentation is maintained in the Project File.

Document Contents:

1. CDD/CDF Data Review Summary Narrative – This narrative is in a letter format to summarize the information pertinent to the samples, methodologies, highlights of findings, and a brief assessment of the overall data quality. For an example, see Attachment III.

2. Summary of Problems and Comments – This document provides checks on the conformance of the QA/QC of the data package to method requirements. A detailed check list for each QA/QC item is included. For an example, see Attachment IV.

3. Checklist for Task Order Compliance – This form details the adherence to the DLM02.0 contract requirements. For an example, see Attachment V.

4. Internal PCDD/PCDF spreadsheet – This form is generated by the data reviewer for data entry into the Element®. It includes the project information, sample information, laboratory data information, the analytes, sample results with appropriate qualifiers, TEQs, and percent moisture. In addition to the standard data qualifiers specified in DLM02.0, Element® qualifiers and remarks are used on this form for entry into Element® to provide more pertinent information for the sample results. In addition, the form includes the reporting limits and calibration ranges to assist data review to apply proper data qualifiers. Water and solid sample results are reported on separate forms. See Attachment VI

5. Copies of Reviewer's Calibration Checks – This documents the checks of the relative response factors (RRFs) for the initial calibrations performed on each primary and confirmation column. The data reviewer should conduct a minimum of one check for each data package.

6. Copies of Reviewer's Sample Result Calculation Checks – This documents the check of the sample results of selected samples in one data package. A minimum of one EMPC value, one EDL value, and one positive result from each of the primary and confirmation analysis should be checked and recorded.

7. PE Score (SPS-Web Form) – This form is generated by the QATS-SPS website program to report the evaluation of the results of the performance evaluation samples (PES) associated with the data package.

8. Communication Documentation, if necessary – Any and all communication(s) with the Contract Laboratory regarding technical and/or contractual issues arising from the validation of the data package must be maintained in the Project File.

9. Data Review Time Tracker – This document is for recording the time line and efforts

at different stages of the data review process. When the data entry into the Element® is required, this form must be executed and included in the data review documents. For an example, see Attachment VII.

10. Data Quality Assessment Report (DQAR) – This report is prepared for non-CLP analysis or projects initiated by the Primary Responsible Parties (PRP). Typically, data for non-CLP and PRP project will not be entered into Element®; therefore, DQAR will replace the Summary of Problems and Comments (item 3), Internal PCDD/PCDF spreadsheet (item 4). In addition, no time tracker (item 9) is required. For an example, see Attachment VIII.

15. Data Reporting

Proper format of results, primary and Element® qualifiers with appropriate remarks should be used for importing the data on the PCDD/PCDF spreadsheet into Element®.

Action:

1. Report the numeric values for all analytes, individual toxicity equivalent quantities (TEQs), and moisture content to 2 significant figures. Reporting units are ng/kg for soils (dry weight) and ng/L for water, respectively. Analytes reported below the CRQL will be considered to be estimated and assigned the "J" flag with the Element® remark "CLP01."

2. Report the value in the scientific expression format "xx E± yy." The number zero (null) should be expressed as 0.0.

3. Report the toxicity equivalent value (TEQ) in the scientific expression format: "xx E± yy" except the values from 0.0 to 9.9 (included).

4. For each analyte that is not detected, an Estimated Detection Limit (EDL) is calculated by the laboratory. For these analytes, report the EDL values and apply the "U" flag.

5. An Estimated Maximum Possible Concentration (EMPC) is calculated and reported by the laboratory when a CDD/CDF has a response with a S/N of at least 2.5 and meets all of the identification criteria with the exception of the ion abundance ratio. For these analytes, report the EMPC value calculated by the laboratory and apply the "U" flag. Indicate that this is an EMPC on the internal CDD/CDF spreadsheet with the Element® qualifier (CLP18).

6. The positive results and non-detects for the homologue totals should be qualified "J" and "UJ," respectively.

7. The homologue totals will not be included in the TEQ calculation.

8. Region 4 qualifiers and remarks applied for CDD/CDF results are summarized below:

Table VII Data Reporting Decision Matrix

Data Quality/Situations		Primary Qualifier	Spreadsheet Entry	Element® Qualifier	Explanation in Summary Report
Not detected (< EDL)		U	-	-	(Not required)
Less than CRQL		J	-	CLP01	(Not required)
PCDPE Interference		U	-	D-4	Ether interference observed for this PCDF
Method Blank (MB)	DL raised	U	-	B-2	Not 5X method blank
	MB gross contamination	R	-	B-1	Gross method blank contamination
	< 1X EMPC MB concentration	U	-	-	(Not required)
Diluted result	> CRQL	-	D	-	(Not required)
	< CRQL	J	D	CLP01	(Not required)
2378-TCDF		See Section 13 of this SOP			
Greater than calibration range		J	-	CLP02	Exceeded calibration range
Erratic initial/continuing calibration RRF		J	-	CLP16	Initial/continuing calibration RRF outside criteria
Homologue totals		J	-	Q-3	(Not required)
PE Score	action low	R (non-detect)	-	CLP06	PE scored action low
		J (positive)	-	CLP06	PE scored action low
	warning low	J (all)	-	CLP07	PE scored warning low
	warning high	J (positive)	-	CLP07	PE scored warning high
	action high	J (positive)	-	CLP08	PE scored action high
Recovery of labeled compounds	low	J (all)	-	QS-3	Labeled compound recovery lower than control limits
	high	J (positive)	-	QS-5	Labeled compound recovery higher than control limits

Table VII Data Reporting Decision Matrix

Data Quality/Situations		Primary Qualifier	Spreadsheet Entry	Element® Qualifier	Explanation in Summary Report
> 10% TEQs from analytes with "J"		J	-	D-5	(Not required)
EMPC		U	-	CLP18	(Not required)
Calibration Evaluation ion ratios not within +/- 15% window		R	-	QC-3	The ion abundance ratio for the calibration standard was within accepted limits.
Technical Holding Time Missed	positive	J	-	H-1	Holding time exceeded
	non-detects	R	-	H-1	Holding time exceeded
OTHERS		Follow National Functional Guidelines			

16. References

1. USEPA Analytical Operations/Data Quality Center (AOC) National Functional Guidelines for Chlorinated Dioxin/Furan Data Review, OSWER 9240.1-37, EPA 540-R-02-003, September 2005.

2. USEPA Contract Laboratory Program Statement of Work For Analysis of Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs), Multi-Media, Multi-Concentration, DLM02.0, May 2005.

3. USEPA Method 1613: Tetra- Through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B, October 1994.

4. USEPA SW846 Method 8290A: Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 1, February 2007.

Attachment I

Primary Data Qualifiers

U The analyte was analyzed for, but was not detected above the Estimated Detection Limit (EDL) as defined in DLM02.0, Exhibit D, Section 11.2.5.

J The analyte was positively identified, but the associated numerical value is an estimated concentration of the analyte in the sample based on its associated quality measures.

N The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."

R The sample result is rejected due to serious deficiencies in the ability to analyze sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Attachment II

Element® Qualifier Definitions

A The analyte was analyzed in replicate. Reported value is an average value of the replicates.

B-1 Analyte is found in the associated blank as well as in the sample (CLP B-flag).

B-2 Reporting level elevated due to trace amounts of analyte present in the method blank.

B-3 Level in blank does not impact data quality

B-4 Level in blank impacts MRLs.

C-1 No sample container received

C-2 Improper sample container used

C-3 Sample container broken on receipt

C-4 Sample container broken in the lab

C-5 EnCore sampler received by the laboratory unlocked

C-6 Sample aliquot taken from VOA vial with headspace (air bubble greater than 5-6 mm diameter).

CL-1 BOD result estimated - Sample exhibited evidence of toxicity

CL-2 DOC result higher than TOC result

CL-3 Sample distillation not required for Ammonia

CLP01 Concentration reported is less than the lowest standard on calibration curve

CLP02 Concentration reported is greater than the highest standard on calibration curve

CLP03 Baseline instability in calibration or preparation blanks

CLP04 Analyte reported as potential false positive (% RSD > 20%, and result > MDL, but < CRQL)

CLP05 CLP ICP-MS method does not include: Al, Ca, Fe, Mg, K, & Na

CLP06 PE sample recovery less than control limits.

CLP07 PE sample recovery outside warning limits.

CLP08 PE sample recovery greater than control limits.

CLP09 MRL elevated due to baseline instability.

CLP10 2,3,7,8-TCDF confirmed by second column.

CLP11 Storage blank contaminant

CLP12 Difference between GC columns above method warning limit

CLP13 Difference between GC columns above method action limit

CLP14 The analysis did not indicate the presence of the analyte. The data is rejected and the reported value is the Reporting Limit. Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

CLP15 TIC Results Reported as Identified by Lab - IDs Not Verified

CLP16 Initial Calibration Response Erratic

CLP17 Initial Calibration Relative Response Outside Method Control Limits

CLP18 Estimated Maximum Possible Concentration (EMPC) Reported

CLP20 Matrix Spike Recovery < 30%

CLP21 %RSD >20% for ICP Multiple Exposures

CLP22 Suspected interference from Al and/or Fe as noted in contractor ICSA solution

CLP23 Suspected over correction from Al and/or Fe as noted in contractor ICSA solution

CLP24 Result has not been confirmed by second column analysis

CR [Custom Value]

D-1 The analyte is determined to be present. The presence of the analyte was confirmed by GC/MS.

D-2 Due to Matrix Interference, the sample cannot be accurately quantified. The reported result is qualitative.

D-3 Sample diluted due to the presence of high levels of non-target analytes resulting in elevated reporting limits.

D-4 MRL elevated due to interferences.

D-5 Estimated quantitation for one or more individual constituents comprising >10% of the total.

F-1 No flash detected up to [Custom Value] °C

F-2 No flash detected up to 60 °C (140 °F).

F-3 Replicates not within method criteria

H-1 Recommended holding time exceeded

H-2 PT or QC sample. Holding time met when calculated from preparation of whole volume.

H-3 PT or QC Sample. Holding time met from beginning of prep.

H-4 Holding time expired prior to receipt by laboratory.

I-1 Ar1242 indistinguishable from 1248 - calculated as Ar1242

I-2 Ar1248 indistinguishable from 1242 - calculated as Ar1248

I-3 Ar1248 indistinguishable from 1254 - calculated as Ar1248

I-4 Ar1254 indistinguishable from 1248 -calculated as Ar1254

I-5 Mixture of Aroclors in sample; predominant Aroclors reported

I-6 Constituents or metabolites of technical chlordane.

J The identification of the analyte is acceptable; the reported value is an estimate.

K The identification of the analyte is acceptable; the reported value may be biased high. The actual value is expected to be less than the reported value.

L The identification of the analyte is acceptable; the reported value may be biased low. The actual value is expected to be greater than the reported value.

MRL-1 MRL verification for Potable Water matrix (Drinking Water)

MRL-2 MRL verification for Non-Potable Water matrix

MRL-3 MRL verification for Soil matrix

MRL-4 MRL verification for Tissue matrix

MRL-5 MRL verification for Air matrix

MRL-6 MRL verification for Waste matrix

MRL-7 MRL Verification for other matrices (bottle blanks, etc)

MRL-8 MRL verification result less than the LOD.

N There is presumptive evidence that the analyte is present; the analyte is reported as a tentative identification.

NA-1 Not Analyzed. Sample lost during preparation or analysis.

NA-2 Not Analyzed. Canister received at 760mm pressure.

NA-3 Not Analyzed. Insufficient sample received for analysis.

NA-4 Not Analyzed or Reported due to Interferences.

NA-5 Not Analyzed. Cannot exceed TCLP regulatory levels based on Total Scan analyses.

NA-6 Not Analyzed. Sample did not flash. Percent Water and Percent Alcohol determinations not required.

NA-7 Not Analyzed. Sample is not aqueous. Percent Alcohol determination not required.

NJ Presumptive evidence that analyte is present; reported as a tentative identification with an estimated value.

P-1 Sample improperly preserved

P-2 Sample at improper pH

P-3 Sample received unpreserved

Q-1 The original extraction of this sample yielded QC recoveries outside control limits. It was re-extracted after the recommended maximum holding time.

Q-2 Result greater than MDL but less than MRL.

Q-3 Instrument not calibrated for all constituents of the total concentration result.

Q-4 Greater than 40 % difference between primary and confirmatory GC columns

Q-5 Serial dilution precision outside method control limits

Q-6 Appropriate QC not prepared and/or analyzed with this sample.

Q-7 Results reported below routine MRL.

QC-1 Analyte low in continuing calibration verification standard

QC-2 Analyte high in continuing calibration verification standard

QC-3 Analyte calibration criteria not met

QC-4 Result greater than the highest point on the calibration curve

QC-5 Calibration check standard less than method control limits.

QC-6 Calibration check standard greater than method control limits.

QI-1 Internal standard was outside of method control limits.

QL-1 Laboratory Control Spike Recovery less than method control limits

QL-2 Laboratory Control Spike Recovery greater than method control limits

QL-3 Laboratory Control Spike Precision outside method control limits

QL-4 Laboratory Control Sample recovery less than 10%

QL-5 Solid (matrix matched) LCS material

QM-1 Matrix Spike Recovery less than method control limits

QM-2 Matrix Spike Recovery greater than method control limits

QM-3 Matrix Spike Precision outside method control limits

QM-4 Matrix Precision outside method control limits

QM-6 Matrix Spike Recovery less than 10%

QM-7 The RPD and/or percent recovery for this QC spike analyte cannot be accurately calculated due to the high concentration of coeluting organic compounds in the sample matrix.

QR-1 MRL verification recovery less than lower control limits.

QR-2 MRL verification recovery greater than upper control limits.

QS-1 Surrogate recovery not calculated due to sample dilution required by high analyte concentration.

QS-2 Surrogate recovery can't be accurately calculated due to interference from coeluting organic compounds.

QS-3 Surrogate recovery is lower than established control limits.

QS-4 Surrogate recovery less than 10%

QS-5 Surrogate recovery is higher than established control limits

R The presence or absence of the analyte can not be determined from the data due to severe quality control problems. The data are rejected and considered unusable.

SP-1 The sample was filtered prior to analysis.

SP-2 Elevated Reporting Limits due to limited sample volume.

TC-2 Insufficient sample for TCLP extraction

TC-3 Results represent analysis of filtrate only

TC-6 Ambient lab temp. during TCLP dropped below method limits.

TC-7 Ambient lab temp. during TCLP exceeded method limits on the high side.

U The analyte was not detected at or above the reporting limit.

X-1 Non-target analyte

X-2 Matrix interference precludes recovery calculation

X-3 Co-eluting/interfering target analyte(s) preclude recovery calculation

X-4 Recovery not calculated due to CCV outside acceptance criteria

X-5 Spiked incorrectly.

X-6 Exclude value from QC data base. Refer to custom remark for details.

XB-1 Carryover from high level sample

XD-1 Duplicate results less than MRL

XD-2 Duplicate results less than 5X MRL

XM-1 Sample background/spike ratio higher than method evaluation criteria

XQ Data is not being reported or may not have been fully reviewed and qualified.

XS-1 Surrogate diluted out due to high analyte concentration

XS-2 Surrogate diluted out due to matrix interference

XS-3 Surrogate not reported due to matrix interference

Y-1 Data reported by memo

Y-2 Data should be limited to screening purposes only

Y-3 No compounds detected in the sample. Second column confirmation not required.

Attachment III

Data Review Summary Narrative

Mr. Charlie Appleby
Environmental Protection Agency, Region 4
Science and Ecosystem Division
980 College Station Road
Athens, GA 30605-2720

SUBJECT: Dioxin Data Review and Validation

Project No. 08-0nnn	ESAT TDF Nos. nnTnnnn
EPA Sample Nos.:	C08xxxxx-0?-0?
Sampling date(s):	08/01/08
With Reference to Site:	Site XYZ., Somewhere, GA
PCDD/PCDF Analyses by:	Contract Laboratory name, City, ST

Dear Mr. Appleby:

The ESAT Work Team reviewed data for the project cited above consisting of six soil samples analyzed per CLP statement of work DLM02.0 for dioxins and furans in one sample delivery group (SDG). The laboratory was submitted both a blind spike and a blind blank PES. The samples were collected on 08/01/08, received by the laboratory on 08/07/08, and the data package was received by USEPA Quality Assurance Section, Region 4 SESD/MTSB on 08/22/08. An email supplement was received on 09/10/08 consisting of continuing calibration, resolution check, and PFK tuning verification to bracket dilutions performed found to be missing by the reviewer in the original submission.

The laboratory prepared and analyzed all samples inside both the contractual and technical holding time limits.

Please refer to the accompanying review document and to the attachments for further details. If you have any questions, please contact this office.

Very Truly Yours:

Name
Sr. ESAT Data Reviewer
ESAT Contractor

Approved:

Name
Region 4 ESAT Team Manager
ESAT Contractor

Attachment IV

Summary of Problems and Comments

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Region 4
Science and Ecosystem Support Division
Office of Quality Assurance
980 College Station Road
Athens, GA 30605-2720

Date: 09/11/08

Subject: Review of Region 4 Dioxin Data
Project No.: nn-nnnn
Laboratory: Analytical Laboratories
Site: Site name
Samples: Water ____ Soil/Sed. X Other ____
Reviewer: Data Reviewer, ESAT Team

I. SUMMARY OF PROBLEMS AND COMMENTS:

1. The laboratory scored within warning limits for all spiked compounds in the PES spike and reported results for all target analytes as nondetects at less than the CRQL in the blind blank PES.

2. All target compounds were reported at concentrations less than the CRQL in the extracted soil method blank. The laboratory reported 2,3,7,8-TCDF as an EDL (monitored ions were just a little less than 2.5X S/N) on the DB-5 column but reported a positive value of 0.160 ng/kg on the DB-225 confirmatory column. The reviewer "U" qualified all 2,3,7,8-TCDF hits that were reported by the laboratory that did not exceed 5X the blank DB-225 result even when reported from the DB-5 column.

3. The laboratory prepared and analyzed all samples inside both the contractual and technical holding time limits.

4. Significant PCDPE interferences (i.e., the monitored ether ions having intensities exceeding approximately 10% of the furan ions) were not observed for target analytes for this project.

5. The OCDD results were "J" qualified in all field samples since the calibration range was always exceeded in the most diluted analytical run. The calculated TEQs were "J" qualified in all field samples because the estimated OCDD contribution always represented more than 10% of the total. However, the SOW does not require that the laboratory perform dilutions for either OCDD or OCDF.

SUMMARY OF DATA REVIEW FOR THIS CASE:

II. ACTUAL SAMPLE HOLDING TIME

Number of Samples	Analysis Late
6	0

REMARKS:

III. MASS RESOLUTION CHECK

OVERALL: A
FREQUENCY: A
IONS MONITORED:
m/z 304.9824: A
m/z 380.9760: A

A - Acceptable - All criteria met, static resolving power demonstrated
P - Provisional - All criteria not met
U - Unacceptable - Criteria not met, static resolving power not demonstrated

REMARKS:

IV. GC COLUMN PERFORMANCE CHECK

OVERALL: A
2378-TCDD VALLEY: A
1289-TCDF/13468-PeCDF S/S: A

A - Acceptable - All criteria met, separation/switching acceptable
P - Provisional - All criteria not met, separation/switching of reasonable quality; data usable.
U - Unacceptable - Criteria not met, separation/switching of poor quality, data unusable

REMARKS:

V. INITIAL CALIBRATION

% RSD: A
S/N RATIO: A
ION RATIO: A

A - Acceptable - All criteria met.
P - Provisional - Some criteria not met, data usable.
U - Unacceptable - Criteria not met, data unusable.

REMARKS:

VI. BEGINNING CONTINUING CALIBRATION CHECK

% D: A

S/N RATIO: A

ION RATIO: A

A - Acceptable - All criteria met.

P - Provisional - Some criteria not met, data usable.

U - Unacceptable - Criteria not met, data unusable.

REMARKS:

VII. ENDING CONTINUING CALIBRATION CHECK

% D: A

S/N RATIO: A

ION RATIO: A

A - Acceptable - All criteria met, static resolving power demonstrated

P - Provisional - All criteria not met

U - Unacceptable - Criteria not met, static resolving power not demonstrated

REMARKS:

VIII. BLANK ANALYSIS

OVERALL: A

FREQUENCY: A

CONTAMINATION: A

A - Acceptable - Contaminants present but below DL

P - Provisional - Contaminants present and above DL but minimal interference with sample results.

U - Unacceptable - Gross contamination, too much interference to use data.

REMARKS:

IX. LABORATORY CONTROL SAMPLE (LCS)

% REC: A

A - Acceptable - All criteria met.

P - Provisional - Some criteria not met, data usable.

U - Unacceptable - Criteria not met, data unusable.

REMARKS:

X. DUPLICATE LABORATORY CONTROL SAMPLE (LCSD)

% REC: A

RPD: A

A - Acceptable - All criteria met.
P - Provisional - Some criteria not met, data usable.
U - Unacceptable - Criteria not met, data unusable.

REMARKS:

XI. BLIND SPIKE RESULTS

PeacTOOLS Results: A

No spike submitted

A - Acceptable - % Recovery acceptable.
P - Provisional - % Recovery > warning limit, data usable.
U - Unacceptable - % Recovery > action limit, data unusable.

REMARKS:

XII. SAMPLE ANALYSES

A. REPORTED ANALYTES

RET TIMES: A
S/N RATIOS A
ION MAX TIME: A
ION RATIO: A
CALCULATIONS: A
PCDPE INT: A

A - Acceptable - All criteria met.
P - Provisional - Some criteria not met, data usable.
U - Unacceptable - Criteria not met, data unusable.

REMARKS:

B. INTERNAL STANDARDS

% RECOVERY: A
S/N RATIO: A
ION RATIO: A

A - Acceptable - All criteria met.
P - Provisional - Some criteria not met, data usable.
U - Unacceptable - Criteria not met, data unusable.

REMARKS:

C. DILUTIONS

OVERALL:	P
ANALYTES	
INT STD:	A
RET TIME:	A
S/N RATIO:	A
ION MAX TIME:	A
ION RATIO:	A
CALCULATIONS:	A
PCDPE INT:	A

A - Acceptable - All criteria met.
P - Provisional - Some criteria not met, data usable.
U - Unacceptable - Criteria not met, data unusable.

REMARKS: The OCDD results were "J" qualified in all field samples since the calibration range was always exceeded in the most diluted analytical run. The calculated TEQs were "J" qualified in all field samples because the estimated OCDD contribution always represented more than 10% of the total. However, the SOW does not require that the laboratory perform dilutions for either OCDD or OCDF.

D. 2378-TCDF CONFIRMATION

MASS RES:	A
GC PERFOR:	A
IN CAL:	A
CON CAL:	A
ANALYTES	
INT STD:	A
RET TIME:	A
S/N RATIO:	A
ION MAX TIME:	A
ION RATIO:	A
CALCULATIONS:	A
PCDPE INT:	A

A - Acceptable - All criteria met.
P - Provisional - Some criteria not met, data usable.
U - Unacceptable - Criteria not met, data unusable.

REMARKS: Only the PES required confirmation.

BLANK SUMMARY FORM					
PCDD/PCDF Data Validation: Method DLM02.0					
Lab ID Description Extract Date Analysis Date Units	LMB????? soil (DB-5) 08/13/08 08/15/08 ng/kg	LMB????? soil (DB-225) 08/13/08 08/20/08 ng/kg			
2,3,7,8 TCDD	ND				
TCDD Total	ND				
1,2,3,7,8 PCDD	ND				
PCDD Total	ND				
1,2,3,4,7,8 HxCDD	ND				
1,2,3,6,7,8 HxCDD	ND				
1,2,3,7,8,9 HxCDD	ND				
HxCDD Total	ND				
1,2,3,4,6,7,8 HpCDD	ND				
HpCDD Total	ND				
OCDD	0.950 J				
2,3,7,8 TCDF	ND	0.160 J			
TCDF Total	0.164				
1,2,3,7,8 PeCDF	ND				
2,3,4,7,8 PeCDF	0.150 JE				
PeCDF Total	ND				
1,2,3,4,7,8 HxCDF	0.292 J				
1,2,3,6,7,8 HxCDF	ND				
1,2,3,7,8,9 HxCDF	ND				
2,3,4,6,7,8 HxCDF	ND				
HxCDF Total	0.484				
1,2,3,4,6,7,8 HpCDF	2.14 J				
1,2,3,4,7,8,9 HpCDF	ND				
HpCDF Total	2.14				
OCDF	4.16J				

REMARKS: E represents EMPC (estimated most probable concentration), ion ratio out.
* High IS recovery.
** Low IS recovery.

Attachment V

Checklist for Task Order Compliance for Dioxin Data Packages delivered under DLM02.0

Regional Tracking Number: **08-0nnn**

SDG No.: **GW-149-0908**

Name of the Reviewer: **ESAT team**

Laboratory Name: **Lab abcd**

Region: **4**

Task Order Number: **EP08W000877**

Date of Review: **October 28, 2008**

1. Task Order Compliance

Check the task order for specific exceptions to the requirements set forth in DLM02.0 for data reporting and the methods of sample preparation, cleanup of sample extracts, and analysis. Check the Task Order (TO) and documentation related to sampling and lab receipt [Chain-of-Custody/Traffic Reports (COC/TR), CDD/CDF Sample Log-in Sheet (DC-1)] to determine the number and identity of the samples that should be present in the Complete Sample Delivery Group (SDG) File (CSF) package. Check the sample documentation to determine the number of matrices present, this should represent the minimum number of preparation batches present in the CSF, and thus the number of method blanks and Laboratory Control Samples (LCS) that should be present.

2. Data Turnaround

On Time?	(Y/N)__N__
If No, Number of days late.	__17___

3. All Forms

Are the following six pieces of information: Lab Name, Lab Code, Case No., Contract, TO No., SDG No., present on all forms?	(Y/N)__N__
Are the values reported for the six items consistent throughout the CSF?	(Y/N)__Y__
Do the reported values agree with the values present on the Task Order and COC/TR documentation?	(Y/N)__Y__

4. Sample Data Summary (Form I-HR CDD-1, 1DFA)

Is a Form 1DFA present for every sample scheduled?	(Y/N)__Y__
Is a Form 1DFA present for each dilution or re-analysis?	(Y/N)_NA__
Is a Form 1DFA present for each DFBLK and LCS?	(Y/N)__N__
Is all header information reported on Form 1DFA	(Y/N)__Y__
Is a concentration or EMPC/EDL present for each target analyte?	(Y/N)__Y__
Is a Peak RT present for each detected target analyte?	(Y/N)__Y__
Is an Ion Ratio present for each target analyte?	(Y/N)__Y__
Are Peak RT, Ion Ratio, and %REC present for each labeled compound?	(Y/N)__Y__
Are all ion ratios and percent recoveries for the labeled compounds within the limits reported on the forms?	(Y/N)__Y__

5. Toxicity Equivalent Summary (Form I-HR CDD-2, 1DFB)

Is a Form 1DFB present for every sample scheduled?	(Y/N)__Y__
Is a Form 1DFB present for each dilution or re-analysis?	(Y/N)__Y__
Is a Form 1DFB present for each DFBLK and LCS?	(Y/N)__N__
Is all header information reported on Form 1DFB	(Y/N)__Y__
Is a concentration (or 0) present on Form 1DFB?	(Y/N)__Y__
Are the TEF-adjusted concentrations present on Form 1DFB?	(Y/N)__Y__
Is the total TEF-adjusted concentration on Form 1DFB?	(Y/N)__Y__

6. CDF Second Column Confirmation (Form I-HR CDD-3, 1DFC)

Is a Form 1DFC present for each Form 1DFA which reports a concentration for 2,3,7,8-TCDF?	(Y/N)_NA__
Is all header information reported on Form 1DFC?	(Y/N)_NA__
Is a concentration or EMPC/EDL present for each target analyte?	(Y/N)_NA__
Is a Peak RT present for each detected target analyte?	(Y/N)_NA__
Is an Ion Ratio present for each target analyte?	(Y/N)_NA__
Are Peak RT, Ion Ratio, and %REC present for each labeled compound	(Y/N)_NA__

7. Total Homologue Concentration Summary (Form II-HR, 2DF)

Is a Form 2DF present for every sample scheduled?	(Y/N)__Y__
Is a Form 2DF present for each dilution and re-analysis?	(Y/N)__Y_
Is a Form 2DF present for each DFBLK and LCS?	(Y/N)__N__
Is all header information reported on Form 2DF?	(Y/N)__Y__
Is the number of peaks present for each homologue?	(Y/N)__Y__
Is a concentration or EMPC/EDL present for each homologue?	(Y/N)__Y__

8. Laboratory Control Sample Summary (Form III-HR, 3DF)

Is a Form 3DF present for each matrix analyzed or preparation?	(Y/N)__Y__
Is all header information reported on Form 3DF?	(Y/N)__Y__
Is the Spike Added present?	(Y/N)__Y__
Is the Amount Recovered present?	(Y/N)__Y__
Is the Percent Recovery Present?	(Y/N)__Y__
Was a LCS prepared and analyzed for each preparation batch?	(Y/N)__Y__
Are less than four compounds outside the recovery limits?	(Y/N)__Y__

9. Method Blank Summary Form (Form IV-HR, 4DF)

Is a Form 4DF present for each matrix analyzed or preparation?	(Y/N)__Y__
Is all header information reported on Form 4DF?	(Y/N) __Y__
Are [EPA Sample No., Lab Sample ID, Lab File ID, Date Analyzed] for each sample associated with the method blank present on Form 4DF?	(Y/N) __Y__
Was a DFBLK prepared and analyzed for each preparation batch?	(Y/N)__Y__
Are all target compounds present in DFBLK at levels <CRQL?	(Y/N)__Y__

10. Window Defining Mix (WDM) Summary (Form V-HR CDD-1, 5DFA)

Is a Form 5DFA present for each analysis of the WDM or the Column Performance Solution (CPS)?	(Y/N)__Y__
Are [GC Column, ID, Lab File ID, Instrument ID, Date Analyzed, Time Analyzed] present for each Form 5DFA?	(Y/N)__Y__
Is RT First Eluting present for each homologue?	(Y/N)__Y__
Is RT Last Eluting present for each homologue?	(Y/N)__Y__
Was the WDM analyzed at the required frequency (beginning and end of each analytical sequence)?	(Y/N)__Y__

11. Chromatographic Resolution Summary (Form V-HR CDD-2, 5DFB)

Is a Form 5DFB present for each analysis of the Isomer Specificity Check (ISC) or CPS? (Y/N)__Y__

Is [GC Column, ID, Lab File ID, Instrument ID, Date Analyzed, Time Analyzed] present for each Form 5DFB? (Y/N)__Y__

Is Percent Valley present for each column used? (Y/N)__Y__

Was the ISC analyzed at the required frequency (beginning and end of each analytical sequence)? (Y/N)__Y__

Was the Percent Valley for the ISC less than 25%? (Y/N)__Y__

12. Analytical Sequence Summary (Form V-HR CDD-3, 5DFC)

Is a Form 5DFC present for each run? (Y/N)__N__

Is [GC Column, ID, Instrument ID, Init. Calib. Date(s), Init. Calib. Times] present on each Form 5DFC? (Y/N)__Y__

Is [EPA Sample No., Lab Sample ID, Lab File ID, Date Analyzed, Time Analyzed] present for each sample in the run? (Y/N)__Y__

13. Initial Calibration Response Factor Summary (Form VI-HR CDD-1, 6DFA)

Is a Form 6DFA present for each initial calibration? (Y/N)__Y__

Is [GC Column, ID, Instrument ID, Init. Calib. Date(s), Init. Calib. Times] present on each Form 6DFA? (Y/N)__Y__

Is RR/RRF present for each target analyte and each labeled compound for each calibration standard? (Y/N)__Y__

Is the mean RR/RRF and %RSD present for each target analyte and each labeled compound? (Y/N)__Y__

14. Initial Calibration Ion Abundance Ratio Summary (Form VI-HR CDD-2, 6DFB)

Is a Form 6DFB present for each initial calibration? (Y/N)__Y__

Is [GC Column, ID, Instrument ID, Init. Calib. Date(s), Init. Calib. Times] present on each Form 6DFB? (Y/N)__Y_

Is the Ion Abundance Ratio present for each target analyte, labeled compound, and internal standard? (Y/N)__Y__

15. Initial Calibration

Was each HRGC/HRMS calibrated prior to analyzing samples?	(Y/N)__Y__
Was calibration performed with at least five standards	(Y/N)__Y__
Were the standards at the required concentrations?	(Y/N)__Y__
Were the %RSD for the RR/RRF within limits?	(Y/N)__Y__
Were the ion abundance ratios within limits?	(Y/N)__Y__

16. Continuing Calibration Summary (Form VII-HR CDD-1, 7DFA)

Is Form 7DFA present for each cont. calibration analyzed?	(Y/N)__Y__
Is [GC Column, ID, Instrument ID, Lab File ID, Date Analyzed, Time Analyzed, Init. Calib. Date(s), Init. Calib. Times] present on each Form 7DFA?	(Y/N)__Y__
Is [RR/RRF, Mean RR/RRF, %D, Ion Ratio] present for each target analyte, labeled compound, clean-up standard, and Internal Standard?	(Y/N)__Y__

17. Continuing Calibration Retention Time Summary (Form VII-HR CDD-2, 7DFB)

Is Form 7DFB present for each cont. calibration analyzed?	(Y/N)__Y__
Is [GC Column, ID, Instrument ID, Lab File ID, Date Analyzed, Time Analyzed, Init. Calib. Date(s), Init. Calib. Times] present on each Form 7DFB?	(Y/N)__Y__
Are the RRT and RT present for each target analyte and labeled compound, and the RT present for the clean-up and Internal Standards?	(Y/N)__Y__

18. Continuing Calibration

Was the calibration monitored at the required frequency?	(Y/N)__Y__
Was the required standard used to monitor the calibration?	(Y/N)__Y__
Were all RRTs within the required limits?	(Y/N)__Y__
Were all %D within the required limits?	(Y/N)__Y__
Were all ion ratios within the required limits?	(Y/N)__Y__

19. Selected Ion Current Profile (SICP) and Data System Reports

Are SICPs and Data System Reports present for each sample, including dilutions, and re-analyses?	(Y/N)__Y__
Are SICPs and Data System Reports present for each Initial Calibration Standard analyzed?	(Y/N)__Y__
Are SICPs and Data System Reports present for each Continuing Calibration Standard analyzed?	(Y/N)__Y__
Are SICPs and Data System Reports present for each DFBLK and LCS analyzed?	(Y/N)__Y__

20. Perfluorokerosene (PFK) Mass Resolution Data

Is PFK data present?	(Y/N)__Y__
Was the PFK tune performed at required frequency?	(Y/N)__Y__

21. Performance Evaluation (PE) Sample Data (if applicable)

Were PE samples analyzed by the laboratory?	(Y/N)_NA_
Were all results within expected windows?	(Y/N)_NA__

22. (3). Lab Code, Contract No. and SDG No. not on forms. (4)., (5)., and (7). Forms not included for LCS. (12). Not for DB-5 ICAL. (Dilutions and TCDF confirmation not required for this SDG).

23. Overall Data Package Acceptable for Payment Purposes Only (Y/N)__Y__

If Not Acceptable for Payment- summary of issues for non-payment.

Attachment VI
Internal PCDD/PCDF Spreadsheet

SOLID	Calibration Stds (pg/uL) TCDD/TCDF	Others	OCDD/OCDF	Equivalent DL in Samples (see units below) TCDD/TCDF	Others	OCDD/OCDF	Equivalent CL in Samples (see units below) TCDD/TCDF	Others	OCDD/OCDF
No dilution:									
(CS1)	0.50	2.50	5.0 ; DL(CS1)=	8.86E-01	4.43E+00	8.86E+00	; CL (CS5)=	3.54E+02	1.77E+03	3.54E+03
(CS5)	200	1000	2000						
Sample wt. = (	13.500	g)	%M or Lipids = (	16.4)		Extract Vol=	(	20) uL		
Extract Diluted :									
Dilution Factor= (	1.0	)	; D_1L(CS1)=	8.86E-01	4.43E+00	8.86E+00	; C_1L (CS5)=	3.54E+02	1.77E+03	3.54E+03

EPA LIMS Sample #:	**Work order-01**	EPA Sample #: SSnnnnn	SDG: SSnnnn		LAB ID #:	Gnnn-nnn-?A
PROJECT NO.:	09-nnnn	Lab: Dioxin Lab	Dioxin Lab 09-nnnn SSnnnnn		Lab File:	a24oct08a_??
PROJECT NAME:	Superfund site				Extraction Date:	10/20/08
DATA REVIEWER:	EPA or ESAT		Method:	CL DLM02.0	Analysis Date:	10/25/08
SAMPLE TYPE:	Soil	X Waste	Fish	Water	Dilution Date	
	ng/KG	ng/Kg	ng/Kg	ng/L		

UNITS: **ng/KG**

	RESULT	CODE		Analysis Date	Element Flag	CRQL			(WHO-TEF) mammals		TEQ mammals	(WHO-TEF) birds	TEQ birds	(WHO-TEF) fish	TEQ fish
401	3.3E-01	U	2,3,7,8 TCDD	10/25/08	CLP18	8.9E-01	x	U,CLP18	1	=	3.3E-01	1	3.3E-01	1	3.3E-01
403	3.2E+00	J	1,2,3,7,8 PeCDD	10/25/08	CLP01	4.4E+00	x	J,CLP01	1	=	3.2E+00	1	3.2E+00	1	3.2E+00
405	7.4E+00		1,2,3,4,7,8 HxCDD	10/25/08		4.4E+00	x		0.1	=	7.4E-01	0.05	3.7E-01	0.5	3.7E+00
406	3.2E+01		1,2,3,6,7,8 HxCDD	10/25/08		4.4E+00	x		0.1	=	3.2E+00	0.01	3.2E-01	0.01	3.2E-01
407	1.7E+01		1,2,3,7,8,9 HxCDD	10/25/08		4.4E+00	x		0.1	=	1.7E+00	0.1	1.7E+00	0.01	1.7E-01
409	9.6E+02		1,2,3,4,6,7,8 HpCDD	10/25/08		4.4E+00	x		0.01	=	9.6E+00	0.001	9.6E-01	0.001	9.6E-01
411	9.7E+03	J	OCDD	10/25/08	CLP02	8.9E+00	x	J,CLP02	0.0003	=	2.9E+00	0.0001	9.7E-01	0.0001	9.7E-01
412	6.9E-01	U	2,3,7,8 TCDF	10/25/08		8.9E-01	x	U	0.1	=	6.9E-02	1	6.9E-01	0.05	3.4E-02
414	1.7E+00	J	1,2,3,7,8 PeCDF	10/25/08	CLP01	4.4E+00	x	J,CLP01	0.03	=	5.1E-02	0.1	1.7E-01	0.05	8.5E-02
415	4.6E+00		2,3,4,7,8 PeCDF	10/25/08		4.4E+00	x		0.3	=	1.4E+00	1	4.6E+00	0.5	2.3E+00
417	2.0E+01		1,2,3,4,7,8 HxCDF	10/25/08		4.4E+00	x		0.1	=	2.0E+00	0.1	2.0E+00	0.1	2.0E+00
418	8.4E+00		1,2,3,6,7,8 HxCDF	10/25/08		4.4E+00	x		0.1	=	8.4E-01	0.1	8.4E-01	0.1	8.4E-01
420	1.2E+01		2,3,4,6,7,8 HxCDF	10/25/08		4.4E+00	x		0.1	=	1.2E+00	0.1	1.2E+00	0.1	1.2E+00
419	3.4E+00	J	1,2,3,7,8,9 HxCDF	10/25/08	CLP01	4.4E+00	x	J,CLP01	0.1	=	3.4E-01	0.1	3.4E-01	0.1	3.4E-01
422	3.9E+02		1,2,3,4,6,7,8 HpCDF	10/25/08		4.4E+00	x		0.01	=	3.9E+00	0.01	3.9E+00	0.01	3.9E+00
423	1.7E+01		1,2,3,4,7,8,9 HpCDF	10/25/08		4.4E+00	x		0.01	=	1.7E-01	0.01	1.7E-01	0.01	1.7E-01
425	9.0E+02		OCDF	10/25/08		8.9E+00	x		0.0003	=	2.7E-01	0.0001	9.0E-02	0.0001	9.0E-02
402	2.7E+00	J	TCDD Total	10/25/08	Q-3	8.9E-01		J,Q-3							
404	2.8E+01	J	PeCDD Total	10/25/08	Q-3	4.4E+00		J,Q-3							
408	2.6E+02	J	HxCDD Total	10/25/08	Q-3	4.4E+00		J,Q-3							
410	2.2E+03	J	HpCDD Total	10/25/08	Q-3	4.4E+00		J,Q-3							
413	1.2E+01	J	TCDF Total	10/25/08	Q-3	8.9E-01		J,Q-3							
416	6.1E+01	J	PeCDF Total	10/25/08	Q-3	4.4E+00		J,Q-3							
421	3.9E+02	J	HxCDF Total	10/25/08	Q-3	4.4E+00		J,Q-3							
424	1.1E+03	J	HpCDF Total	10/25/08	Q-3	4.4E+00		J,Q-3							
430	**3.2E+01**	J	TEO (mammals from 2005 WHO-TEF	10/25/08	D-5	3.2E+01		J,D-5							
428	**2.2E+01**	J	TEO (avian from 1998 WHO-TEF)	10/25/08	D-5	2.2E+01		J,D-5							
429	**2.0E+01**	J	TEO (fish from 1998 WHO-TEF)	10/25/08	D-5	2.0E+01		J,D-5							
9999	1.6E+01		% moisture	10/25/08											
			% Lipids												

Attachment VII

TIME TRACKER

VERSION 4.0

CASE # : NA PROJECT #: 08-0nnn TDF NO: 08Tnnnn

LAB METHOD(S): DLM02.0

NUMBER OF SAMPLES: 8 VALIDATED TIME OF SAMPLE RECEIPT (VTSR): 08/07/08 DUE DATE: 09/24/08

SITE NAME: Superfund Site Co. SITE ID: 0???

Box Inventory 08-122 PROGRAM: SARA TASK ORDER: **Ennn- 001 -42**

	STAGE OR PERSON		INITIALS	DATE ACCEPTED	COMPLETION DATE	# Hours
1.	Received by EPA OQADI			08/22/08		
2.	Evidentiary Audit		Initials	08/26/08	08/27/08	1.5
3.	Data Reviewer		Initials	09/08/08	09/11/08	12
4.	Data Entry	Initial Data Entry				electronic
		Data and Qualifiers Corrections (if any)				
5.	LIMS Data Verification	Initial Data				NA
		Corrections (if any)				

6. Task Monitor (Overview /data distribution)

Sample and Method Information

EPA Samples # (Separated by methods for cases with multiple lab methods applied)	V	SV	Pest./ PCB	PCDD/ PCDF	Metals		CN	OTHERS (specified)
					ICP/AES	ICP/MS		
C0nnnnn-01-08				X				

Notes/Comments

Attachment VIII

Data Quality Assessment Record: PCDD/PCDF

Review Date: _____ **Analysis Date:** _____ **Matrix:** _____ **Activity #:** _____

Activity Name: _____

Method: 8290 _____ M23 _____ CLP _____ Other (specify) _____

Signatures Analyst _____ Reviewer _____
(or contract laboratory data reviewer)

(An explanation for any "no" answer must be provided)

		Yes	No	N/A
1.	**Holding Times: (§6.4, 8290)**			
	- PCDDs/PCDFs extracted within 30 days of sampling?	___	___	___
	- Extracts analyzed within 40 days of extraction?	___	___	___
	- Were all samples/extracts properly preserved?	___	___	___
2.	**Laboratory Documentation**			
	- Sample Custody documented?	___	___	___
	- Spiking Standards Traceable?	___	___	___
	- Spiked amounts documented?	___	___	___
	- Sample preparation steps documented, including all clean-up steps?	___	___	___
	- Calibration standards traceable?	___	___	___
3.	**GC/MS Tuning: (§7.6, 8290)**			
	- MS operated in SIM mode, ≥ 1 cycle/sec?	___	___	___
	-At least all 48 ions in Table 6, in 4 or 5 groups? (Tetra & Penta can be combined)	___	___	___
	- Same set of ions monitored for std and sample analyses?	___	___	___
	-Tune to 10,000 resolution @ 10% valley, using PFK ion @ 304.9824?	___	___	___
	-Verify exact mass of m/z 380.9760? Note whatever m/z's are chosen for tuning, m/z difference must be ≤ the largest range in any of the descriptor groups.	___	___	___
4.	**Initial Calibration: (§ 7.7, 8290)** Instrument: _____			
	3.1 Procedure:			
-	Begun with column performance check sol (Table 7, 8290).	___	___	___
	- Checks 1st and last ions in each descriptor, as well as TCDD isomer chromatographic resolution.	___	___	___

	Yes	No	N/A
- Acquire data for 2 ul of each of 5 levels, as in Table 5, 8290.	___	___	___
- The ratio of integrated ion currents must be within limits of Table 8, 8290 (both labeled and non-labeled).	___	___	___
- Referring to Table 9, 8290, calculate RRFs for the 17 unlabeled target analytes relative to their ISs (Table 5, and for the 9 $^{13}C_{12}$-labeled ISs relative to the two recovery standards (Table 5).	___	___	___
- Calculate Mean RF and %RSD for each of 5 levels of standard (2,3,7,8-substituted isomers, as in Table 9).	___	___	___
- Calculate RRFs for total isomers in each homologous series according to 7.7.1.4.6.	___	___	___
- For series which contain only one isomer (i.e. OCDD, OCDF) or only one 2,3,7,8 isomer (i.e. TCDD, TCDF, PeCDD, & HpCDD), use the mean RRF calc'd in 7.7.1.4.5.	___	___	___
- For series which contain more than 1 2,3,7,8-substituted isomer, use the average of the RFs for the 2,3,7,8 isomers in that group (see 7.7.1.4.6.2).	___	___	___
- Calculate mean RFs for the nine ISs, rel. to the Recovery Stds from the 5 levels.	___	___	___
4.2 Initial Cal Acceptance Criteria:			
- %RSDs for mean RFs of 17 unlabeled 2,3,7,8 analytes ≤20%?	___	___	___
- %RSDs for mean RFs of 9 labeled ISs ≤30%?	___	___	___
- S/N ratios for the GC signals in <u>every</u> std SICP ≥10?	___	___	___
- The ion abundance ratios (Table 8, 8290) within limits?	___	___	___
5. Analysis (Refer to Figure 3, 8290):			
- Laboratory documentation should show that extracts were removed from storage and allowed to warm to room temp.	___	___	___
- Each daily run must begin with a MS resolution check, column performance check, a continuing cal, and a method blank.	___	___	___
- Column Performance Check (§ 8.2.1)			
- Chrom separation between 2,3,7,8 isomers ≤25% valley.	___	___	___
- Verify presence of 1,2,8,9-TCDD and 1,3,4,6,8-PeCDF and 1st & last eluters of each group.	___	___	___
- <u>All</u> peaks should be labeled on chromatograms.	___	___	___
- First & last eluters should be denoted on chrom with a "F" or "L".	___	___	___
- An individual SICP of two ions or reconstructed ion current profile of each series must be part of data.	___	___	___
- Run times of switching groups must			

appear of the SICPs. ___ ___ ___

	Yes	No	N/A
- Absolute RT of mixture components within 10 sec. of method, to assure accurate group switching.	___	___	___
- Static resolving power check before each run? (recommended)	___	___	___
- Static resolving power check only 1 per 12-hour run? (required)	___	___	___

- Lock mass ion monitored, @ approx 10% scale?
- M/Zs Monitored

303.9016	351.9000	389.8156	435.8169
305.8987	353.8970	391.8127	479.7165
315.9419	355.8546	401.8559	[430.9728]
317.9389	357.8516	403.8529	441.7428
319.8965	367.8949	445.7555	443.7399
321.8936	369.8919	[430.9728]	457.7377
331.9368	409.7974	407.7818	459.7348
333.9338	[354.9792]	409.7788	469.7780
375.8364	373.8208	417.8250	471.7750
[354.9792]	375.8178	419.8220	513.6775
339.8597	383.8639	423.7767	[442.9728]
341.8567	385.8610	425.7737	

Continuing Calibration Check (HRCC-3, Table 5, 8290).

	Yes	N/A	No
- %D of RFs for unlabeled analytes ≤20%	___	___	___
- %D of RFs for labeled ISs ≤30%	___	___	___
- Ion abundance ratios as per Table 8, 8290.	___	___	___
- If either %D criteria is not met, repeat <u>one time</u>	___	___	___
- Use judgment vs. project goals or recalibrate.	___	___	___

- Sample Analysis

- S/N ratio ≥2.5?	___	___	___
- S/N ratio printed next to peak (with S/N <5:1).	___	___	___
- Retention time of analytes with accompanying spiked labeled congeners within -1 to +3 sec?	___	___	___
- Retention time of 2,3,7,8-substituted analytes with no labeled analog present within 0.005 RRT units?	___	___	___
- Retention time of non-2,3,7,8-substituted analytes within RT window of homologous series?	___	___	___
- Ion current maxima for both quant ions occurring within ±2 sec? (applies to labeled and unlabeled analogs).	___	___	___
- Ion abundance criteria met per Table 8?	___	___	___

	Yes	No	N/A
- signal observed at same RT on diphenyl ether channel? (Table 6, 8290).	___	___	___
- Continuing Cal and Column MS resolution check run at end of each 12-hour period?	___	___	___
- If lab operates consecutive 12-hour periods, run col. perf. check between.	___	___	___
6. Spikes:			
- Was a method spike analysis performed?	___	___	___
- Were matrix spike duplicate analyses performed?	___	___	___
- Were acceptable recoveries obtained?	___	___	___
7. Laboratory Duplicate:			
- %RPD within limits?	___	___	___
8. Blanks:			
- Were method blank analyses performed?	___	___	___
- Were any contaminants noted?	___	___	___
- If yes, were blank rules applied to the data?	___	___	___
9. Performance Evaluation Sample:			
- Was a P.E. Sample analyzed with the samples?	___	___	___
- If yes, were acceptable results obtained?	___	___	___
10. Internal Standard Response			
- % Recovery between 40% and 135%?	___	___	___
11. Surrogates (Added at start of sample prep):			
- Were surrogate recoveries acceptable?	___	___	___

Additional Comments: